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(54) Title: AN ADIABATIC PROCESS FOR THE PREPARATION OF ION EXCHANGE AND ADSORBENT COPO- LYMERS (57) Abstract Crosslinked copolymer beads suitable for making polymeric adsorbents and ion-exchange resins are prepared by a substantially adiabatic suspension copolymerization of at least one monoethylenically unsaturated monomer with at least one polyethylenically unsaturated monomer in the presence of an effective amount of free-radical polymerization initiators.		

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AN ADIABATIC PROCESS FOR THE PREPARATION OF ION EXCHANGE AND ADSORBENT COPOLYMERS

Ion-exchange resins are used by industry to separate chemical species from solutions containing them. Such resins are prepared by substituting various functional groups onto a copolymer bead matrix. The functional groups are capable of associating with the impurities so as to remove them from solution. Ion-exchange resins may be cation-, anion-, or chelate-exchange resins, depending on the choice of functional group substituted onto the copolymer bead matrix. The copolymer bead matrix may also be used in preparing polymeric adsorbents, such as those disclosed in U.S. Patent 4,950,332.

The copolymer bead matrix is typically prepared by suspension polymerization of a finely divided organic phase comprising monovinylidene monomers like styrene, polyvinylidene monomers such as divinylbenzene, a free-radical initiator, and, optionally diluents which are either phase-separating or soluble; see, for example, U.S. Patent 4,224,415. The copolymer beads produced may be microporous, i.e., gellular in character, or macroporous, the result depending upon whether the phase-separating diluent is employed. The term "macroporous" as commonly used in the art means that the copolymer has both macropores and mesopores. The terms "microporous", "gel", and "macroporous" are well known in the art and generally describe the nature of the copolymer bead porosity. Microporous or gel copolymer beads have pore sizes on the order of less than 20 Angstroms (\AA), while macroporous copolymer beads have both mesopores of from 20 \AA to 500 \AA and macropores of greater than 500 \AA . Gel and macroporous copolymer beads, as well as their preparation, are further discussed in U.S. Patent 4,256,840.

Recently, industry has focused on methods of preparing copolymer beads in multi-staged polymerizations, also known as seeded polymerization processes. Such copolymer beads are desirable due to good mechanical strength and osmotic shock resistance. Seeded polymerization processes can also prepare beads of relatively uniform size if the seed particles employed have similar size uniformity. U.S. Patents 4,419,245 and 4,564,644 disclose processes wherein seed particles are suspended in a continuous medium and, thereafter, the seed particles are imbibed and polymerized with additional monomer to form copolymer beads. British Patent 1,151,480 discloses a process wherein copolymer beads are prepared from porous seed particles. European Patent Application Publication No. 0 062 088 discloses the preparation of gel or macroporous copolymer beads by a seeded polymerization process and European Patent Application Publication No. 0 168 622 describes the preparation of macroporous copolymer beads by a seeded polymerization process using macroporous seed particles.

Crosslinked copolymers for ion exchange and absorbent resins are conventionally prepared by suspension polymerization with one to three isothermal stages wherein the heat generated by the polymerization exotherm is removed to maintain the isothermal conditions.

The prior art conventional technology requires a long cycle time of 10-20 hours per batch and generates high polymer waste, especially with low crosslink recipes. In addition, reactors require excess heat removal capacity to maintain the isothermal conditions.

U.S. Patent 4,239,669 teaches the emulsion polymerization of vinyl aromatic
5 monomer and conjugated diene under adiabatic conditions in a continuous flow agitated reactor. The phase ratio is held low to hold the temperature to 80-100°C. The emulsion particle size is 1000-1500 Å. This patent does not refer to the preparation of a suspension bead product and the particles produced are not hard crosslinked bead polymer used in the production of ion exchange resins.

10 This invention concerns the preparation of ion exchange copolymers characterized by polymerizing the monomer phase in the presence of the aqueous phase under substantially adiabatic conditions. A substantial amount of the heat of polymerization is not removed but is used to raise the temperature of the reactor contents. Reaction kinetics are substantially accelerated resulting in a very short polymerization time at the final adiabatic
15 temperature, resulting in better reactor utilization and increased product throughput. In addition, less reactor waste is generated leading to cleaner reactors and less downtime.

More particularly, the present invention concerns a process for making crosslinked copolymer beads suitable for polymeric adsorbents and ion-exchange resins characterized by:

- 20 (a) providing a suspension of a monomer mixture within a continuous suspending medium, the monomer mixture comprising at least one monoethylenically unsaturated monomer selected from styrene, vinyl toluene, vinylbenzyl chloride or ethylvinylbenzene, at least one polyethylenically unsaturated monomer selected from divinylbenzene, ethylene glycol diacrylate,
25 ethylene glycol dimethacrylate or mixtures thereof, and an effective amount of free-radical polymerization initiator;
- (b) maintaining the suspension under conditions sufficient to polymerize the monomer mixture and obtain copolymer beads, the conditions including retention within the suspension of a substantial amount of exothermic heat
30 evolved during polymerization of the monomers to copolymer, the retention of the exothermic heat resulting in a rise in temperature of the suspension to at least 120°C for a time sufficient to polymerize to substantially complete conversion; and
- (c) recovering the copolymer beads from the suspension.

35 Polyethylenically unsaturated monomers useful in the present invention include, for example, divinylbenzene, ethylene glycol diacrylate and ethylene glycol dimethacrylate. Such monomers are advantageously present in an amount of from 0.04 to 80 weight percent based on total weight of the monomer mixture. Monoethylenically unsaturated monomers

include, for example, styrene, paravinyltoluene, vinyltoluene, vinylbenzyl chloride and ethylvinylbenzene. Such monomers are advantageously present in an amount of from 20 to 99.96 weight percent based on the total weight of the monomer mixture. With aromatic and acrylate monomers the conversion is preferably in excess of 97 weight percent.

5 The free-radical initiator employed is advantageously selected from peroxides, peroxyesters and azo compounds such as, for example, benzoyl peroxide, *t*-butyl peroctoate and *t*-butyl perbenzoate. The initiator is advantageously employed in an effective amount of from at least 0.05 weight percent to 2.0 weight percent based on the weight of the monomers.

 The monomers can be added to the suspending medium in an inert diluent such
10 as, for example, *iso*-octane, amyl alcohol, *t*-butyl alcohol, *sec*-butyl alcohol and toluene. The suspending medium is preferably water containing suspending agents such as, for example, gelatins, carboxymethyl methylcellulose, polyvinyl alcohols, inorganic stabilizers such as tricalcium phosphate, bentonite clays and zinc hydroxides. The monomers can be imbibed into a seed polymer or a portion of the monomer can be added intermittently or continuously as the
15 polymerization proceeds. For seeded recipes surfactants such as sodium lauryl sulfate are advantageously employed. The suspension is advantageously maintained at an initial temperature of at least 40°C, preferably at least 70°C by applying heat from an external source until the exothermic heat evolved from polymerization of the monomers to copolymer is sufficient to at least maintain the polymerization without further addition of heat to the
20 suspension. During the reaction the temperature of the suspension advantageously reaches at least 120°C and preferably at least 130°C for a time sufficient to polymerize at least 90 weight percent (preferably at least 99.5 weight percent) of the polymerizable monomer.

 Some moderate lowering of the final temperature may be achieved by employing polymerization moderators, such as, for example, α -methylstyrene and by partial removal of
25 heat through the jacket of the reactor, thereby increasing the phase ratio of the reaction mixture. The sensible heat of feed streams into the reactor can also be advantageously used to moderate the final temperature and thus the phase ratio.

 The invention is further illustrated by the following example in which the quantities are given in parts by weight unless otherwise indicated.

30 Example 1

 Batch polymerizations were conducted in a 1-gallon stainless steel jacketed reactor equipped with agitation. The monomer phase was comprised of 683.6 g styrene, 116.4 g 55 percent divinylbenzene (DVB-55), 8 g 50 percent *t*-butyl peroctoate and 0.4 g *t*-butyl perbenzoate. The aqueous phase was comprised of 1276 g water, 320 g 1 percent
35 carboxymethyl methylcellulose (suspending agent) and 4 g 60 percent sodium dichromate (latex polymerization inhibitor). The weight phase ratio (monomer:aqueous) was 1:2. Both phases were loaded into the reactor, which was then sealed and pressure tested. The reactor was purged with nitrogen and the agitation rpm was set. The reactor temperature was ramped

to 80°C to initiate the monomer charge and heated as fast as possible, about one-half hour, to the final adiabatic temperature (130°C) to simulate the self-heat ramp. The reactor was held at that temperature for 1 hour and then cooled. The copolymer was unloaded, washed, filtered, dried, and sieved. The copolymer of Example 1 was functionalized by sulfonating the beads
5 with an excess of 99 percent sulfuric acid utilizing methylene chloride as the swelling solvent. The sulfonated beads were hydrated with increasingly diluted sulfuric acid and then backwashed with deionized water to form a strong acid gel cation exchange resin.

The final properties of the resin obtained were:

Whole Perfect Beads (WPB) = 99%
10 Water Retention Capacity = 50.4%
Dry Weight Capacity = 5.2 meq/g
Wet Volume Capacity = 2.0 meq/ml
Crush Strength = 1290 g/bead
Osmotic Shock Resistance = 90% WPB*

15 *The percentage of whole perfect beads after 25 cycles of successive washes as follows: 1) 10 percent sodium hydroxide, 2) water, 3) 10 percent sulfuric acid, and 4) water.

The final resin properties from the adiabatic polymerization are comparable or superior to those of resins produced conventionally.

Water retention capacity is determined by swelling a weighed amount of resin
20 with water, removing excess water and weighing the fully swollen resin. The resin is then dried on a moisture balance until a constant weight is obtained. Water retention capacity is the ratio of water imbibed to the total combined weight of the resin plus imbibed water.

Dry weight capacity, weak-base capacity, salt-splitting capacity and wet volume capacity are determined by standard analytical techniques. Crush strength is determined by
25 taking a statistically representative sample of at least 30 beads from a given sample of resin or copolymer beads, and determining the force, in grams, needed to fracture each bead using a Chatillon Scale, Model DPP-1KG available from J. Chatillon & Sons Company. Crush resistance is reported as the average of the force measurements obtained for the 30 beads.

Example 2

30 The procedure of Example 1 was repeated except that the initiator employed was 5.6 g benzoyl peroxide. The weight phase ratio (monomer:aqueous) was 1:2.

The final properties of the strong acid gel cation exchange resin obtained were:

Whole Perfect Beads (WPB) = 99%
Water Retention Capacity = 50.8%
35 Dry Weight Capacity = 5.3 meq/g
Wet Volume Capacity = 1.9 meq/ml
Crush Strength = 1840 g/bead
Osmotic Shock Resistance = 97% WPB

Example 3

Using the same procedure set forth in Example 1, another batch polymerization was conducted to synthesize a gel copolymer. The monomer phase was comprised of 779.8 g styrene, 19.9 g DVB-55, and 10.9 g benzoyl peroxide. The aqueous phase was comprised of
5 1313 g water, 287 g 1 percent carboxymethyl methylcellulose, 2.5 g 60 percent sodium dichromate. The weight phase ratio (monomer:aqueous) was 1:2. The copolymer of Example 3 was functionalized by chloromethylating the beads with an excess of chloromethylmethyl ether in the presence of ferric chloride catalyst. The excess ether was destroyed with three methanol washes. The chloromethylated beads were then swollen in methanol and reacted
10 with trimethylamine to form a strong base gel anion exchange resin. The final anion resin properties were:

Whole Perfect Beads (WPB) = 99%

Water Retention Capacity = 76.7%

Dry Weight Capacity = 4.3 meq/g

15 Wet Volume Capacity = 0.65 meq/ml

Example 4

Following the procedure of Example 1, another batch polymerization was conducted to synthesize a macroporous copolymer. The monomer phase was comprised of 506 g styrene, 208 g DVB-55, 284 g *iso*-octane, 3.6 g 50 percent *t*-butyl peroctoate and 1.2 g
20 *t*-butyl perbenzoate. The aqueous phase was comprised of 1182 g water, 314 g 1 percent carboxymethyl methylcellulose and 3.2 g 60 percent sodium dichromate. The weight phase ratio (organic:aqueous) was 2:3. The copolymer beads were washed and then steam distilled to remove the *iso*-octane, and dried before functionalization. The copolymer of Example 4 was functionalized by sulfonating the beads with an excess of 99 percent sulfuric acid. The
25 sulfonated beads were hydrated with increasingly diluted sulfuric acid and then backwashed with deionized water to form a strong acid macroporous cation exchange resin. The final cation resin properties were:

Whole Perfect Beads (WPB) = 99%

Water Retention Capacity = 47.0% (Na⁺)

30 Wet Volume Capacity = 2.1 meq/ml (Na⁺)

Example 5

Following the procedure of Example 4, another batch polymerization was conducted to synthesize a macroporous copolymer. The monomer phase was comprised of 692.4 g styrene, 107.6 g DVB-55, 490 g *iso*-octane, 7.2 g 50 percent *t*-butyl peroctoate and 4.8 g
35 *t*-butyl perbenzoate. The aqueous phase was comprised of 1005 g water, 271 g 1 percent carboxymethyl methylcellulose and 2.7 g 60 percent sodium dichromate. The weight phase ratio (organic:aqueous) was 1:1. The copolymer of Example 5 was functionalized by chloromethylating the beads with an excess of chloromethylmethyl ether in the presence of

ferric chloride catalyst. The chloromethylated beads were washed with methanol three times and then reacted with dimethylamine to form a weak base macroporous anion exchange resin.

The final anion resin properties were:

- Whole Perfect Beads (WPB) = 99%
- 5 Water Retention Capacity = 43.3%
- Dry Weight Capacity = 5.5 meq/g
- Wet Volume Capacity = 2.0 meq/ml
- Weak Base Capacity = 1.8 meq/ml
- Salt Splitting Capacity = 0.2 meq/ml

10 Example 6

- Batch polymerizations were conducted in a 30-gallon stainless steel jacketed reactor equipped with agitation. The organic phase was comprised of 24.6 kg styrene, 5.1 kg DVB-55, 64.6 g 50 percent *t*-butyl peroctoate and 14.4 g *t*-butyl perbenzoate. The aqueous phase was comprised of 46.4 kg water, 19.1 kg 0.5 percent carboxymethyl methylcellulose (suspending agent), 163.8 g 60 percent sodium dichromate (latex inhibitor). The mass phase ratio (monomer:aqueous) was 0.45. The reactor was heated from room temperature to 80°C to initiate the monomer charge and allowed to self heat thereafter to the final adiabatic temperature (130°C). The reactor was held at that temperature for 1 hour and then cooled. The copolymer was unloaded, washed, filtered, dried, sieved, and then sulfonated as in
- 20 Example 1 to form a strong acid gel cation exchange resin. The final cation resin properties were:

- Whole Perfect Beads (WPB) = 99%
- Water Retention Capacity = 47.9%
- Wet Volume Capacity = 2.2 meq/ml
- 25 Dry Weight Capacity = 5.3 meq/g
- Crush Strength = 1480 g/bead
- Osmotic Shock Resistance = 96%

The final resin properties with the adiabatic polymerization are comparable or superior to that of resins produced conventionally.

30 Example 7

- Batch seeded polymerizations were conducted in a 1-gallon stainless steel jacketed reactor equipped with agitation. Polystyrene seeds (100 g) containing 0.3 percent DVB-55 were suspended in 1000 g deionized water. The monomer phase comprised of 50 g DVB-55, 650 g styrene and 2.4 g 50 percent *t*-butyl peroctoate and 1.2 g *t*-butyl perbenzoate
- 35 was added to the reactor and agitated (rpm = 220) for 1 hour. A mixture comprised of 0.8 g 30 percent sodium lauryl sulfate and 40 g deionized water was added and mixed for 30 min. The aqueous phase comprised of 320 g 1 percent carboxymethyl methylcellulose, 3 g 60 percent sodium dichromate solution and 500 g deionied water was added and allowed to mix well. The

reactor was ramped from room temperature to 80°C to initiate the monomer charge and was heated as fast as possible, in about 1/2 hour, to the final adiabatic temperature (130°C) to simulate the self heat ramp. The reactor was held at that temperature for 2 hr and then cooled. The copolymer was unloaded, washed, filtered, dried and sieved.

- 5 The average seed size determined by microscopy was 220 microns (μ) and the average copolymer size was 425 μ , which corresponds to a grow-up of 1.93. The expected grow-up based on the monomers and seed charged is 2.0 which indicates that the seed did imbibe the monomer, with minimal second generation particle formation.

- Sulfonations were performed conventionally in 1-liter glass reactors equipped
10 with agitation. Copolymer (60 g) was sulfonated with 480 g 99 percent sulfuric acid and 27 ml methylene chloride (swelling agent). The copolymer was swollen for 30 min and sulfonated for 2 hours at 130°C. The sulfonated resin was hydrated by progressively washing the beads with decreasing concentrations of sulfuric acid and backwashed with deionized water. The final resin properties were:

- 15 Water Retention Capacity (WRC) : 78.4%
 Dry Weight Capacity (DWC) : 5.3 meq/g
 Wet Volume Capacity (WVC) : 1.2 meq/ml

Example 8

- Batch seeded polymerizations were conducted in a 1-gallon stainless steel
20 jacketed reactor equipped with agitation. Polystyrene seeds (48.6 g) containing 50 percent isobornyl methacrylate and 0.05 percent DVB-55 were suspended in 500 g deionized water. The monomer phase comprised of 29 g DVB-55, 171 g styrene, 200 g commercial-grade iso-octane and 3.0 g 50 percent t-butyl peroctoate and 0.6 g t-butyl perbenzoate was added to the reactor and agitated (rpm = 230) for 2 hours. A mixture comprised of 428 g 1 percent
25 carboxymethyl methylcellulose, 2.2 g 60 percent sodium dichromate solution and 573 g deionized water was added and allowed to mix well. The reactor was ramped from room temperature to 80°C to initiate the monomer charge and heated as fast as possible, in about 1/2 hr, to the final adiabatic temperature (130°C) to simulate the self heat ramp. The reactor was held at that temperature for 2 hr and then cooled. The copolymer was unloaded, washed,
30 filtered, air-dried and sieved.

 The copolymer beads were smooth and opaque. The single point BET surface area was determined to be 25 sq m/g. Most of the pores were $>300\text{\AA}$. The pore volume was 0.5 cc/g, indicating macroporosity.

Example 9

- 35 Batch, continuous-addition, seeded polymerizations were conducted in a 1-gallon stainless steel jacketed reactor equipped with agitation. A mixture comprised of 843.4 g deionized water, 4.1 g 60 percent sodium dichromate solution and 2.7 g 1 percent sodium lauryl sulfate solution was added to the stirred reactor (rpm = 220) with 261.9 g of polystyrene

seed containing 0.3 percent DVB-55. The monomer phase comprised of 40.5 g DVB-55, 284.3 g styrene and 3.2 g 50 percent *t*-butyl peroctoate and 1.6 g *t*-butyl perbenzoate was also added to the reactor and agitated for 1 hour. The aqueous phase comprised of 1.7 g gelatin A, 1.7 g gelatin B and 3.9 g 10 percent sodium lauryl sulfate dissolved in 247.3 g hot deionized water was added to the reactor to disperse the swollen seed. The reactor was ramped from room temperature to 80°C to initiate the monomer charge. After a 1/2 hr hold at temperature, the con-add phase comprised of 683.7 g styrene and 38.7 g DVB-55 was added over a 1/2 hour time period. The reactor was simultaneously heated as fast as possible, in about 1/2 hr, to the final adiabatic temperature (140°C) to simulate the self heat ramp. The reactor was held at that temperature for 1 hr and then cooled. The copolymer was unloaded, washed, filtered, dried and sieved.

The volume median seed size was determined as 214 μ and the volume median copolymer size was 346 μ , which corresponds to a grow-up of 1.62. The expected grow-up based on the monomers and seed charged is 1.7 which indicates that the seed did imbibe the monomer, with minimal second generation particles formation.

The sulfonations were performed as in Example 7 to form a strong acid gel cation exchange resin. The final resin properties were:

Water Retention Capacity (WRC) : 63.8%

Dry Weight Capacity (DWC) : 5.3 meq/g

Wet Volume Capacity (WVC) : 1.4 meq/ml

The water retention capacity for a strong acid sulfonic exchanger is a function of the DVB crosslinkage. For the 3.3 percent crosslink level of this recipe, the WRC for a standard non seeded resin is 75 percent [Ref: *Ion Exchangers*, Ed. K. Dorfner, W.de Gruyter & Co, Berlin, 1991]. The WRC data confirms that the effective crosslink density of the seeded resin is more than that of a nonseeded resin with the same crosslink level.

Example 10

Batch, in situ, continuous-addition, seeded polymerizations were conducted in a 1-gallon stainless steel jacketed reactor equipped with agitation. The aqueous phase comprised of 1000 g deionized water, 250 g 1 percent carboxymethyl methylcellulose and 3.1 g 60 percent sodium dichromate solution was added to a stirred reactor (rpm = 220). The monomer phase comprised of 49.7 g DVB-55, 341 g styrene, 2.5 g 78 percent benzoyl peroxide and 2.0 g *t*-butyl perbenzoate was also added to the reactor. The droplets were sized for 30 minutes. The reactor was ramped from room temperature to 80°C to initiate the monomer charge. After a 1/2 hour hold at temperature, the con-add phase comprised of 235 g styrene and 23.5 g DVB-55 was added over a 1/2 hour time period. The reactor was simultaneously heated as fast as possible, in about 1/2 hr, to the final adiabatic temperature (130°C) to simulate the self heat ramp. The reactor was held at that temperature for 2 hr and then cooled. The copolymer was unloaded, washed, filtered, dried and sieved.

The sulfonations were performed as in Example 7 to form a strong acid gel cation exchange resin. The final resin properties were:

Water Retention Capacity (WRC) : 49.4%

Dry Weight Capacity (DWC) : 5.1 meq/g

5 Wet Volume Capacity (WVC) : 2.2 meq/ml

The water retention capacity for a strong acid sulfonic exchanger is a function of the DVB crosslinkage. For the 6.2 percent crosslink level of this recipe, the WRC for a standard non seeded resin is 60.5 percent. The WRC data confirms that the effective crosslink density of the seeded resin is more than that of a nonseeded resin with the same crosslink level.

10 The final resin properties with the adiabatic polymerization are comparable or superior to that of resins produced conventionally.

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CLAIMS

1. A process for making crosslinked copolymer beads suitable for making polymeric adsorbents and ion-exchange resins characterized by:
 - (a) providing a suspension of a monomer mixture within a continuous suspending medium, the monomer mixture comprising at least one
5 monoethylenically unsaturated monomer selected from styrene, vinyl toluene, vinylbenzyl chloride or ethylvinylbenzene, at least one polyethylenically unsaturated monomer selected from divinylbenzene, ethylene glycol diacrylate, ethylene glycol dimethacrylate or mixtures thereof, and an effective amount of free-radical polymerization initiator;
 - (b) maintaining the suspension under conditions sufficient to polymerize the
10 monomer mixture and obtain copolymer beads, the conditions including retention within the suspension of a substantial amount of exothermic heat evolved during polymerization of the monomers to copolymer, the retention of the exothermic heat resulting in a rise in temperature of the suspension to at least
15 120°C for a time sufficient to polymerize to substantially complete conversion; and
 - (c) recovering the copolymer beads from the suspension.
2. The process of Claim 1 wherein the suspension reaches a temperature of at least 130°C.
- 20 3. The process of Claim 1 wherein the suspension is at a temperature of at least 120°C for a time sufficient to polymerize at least 90 weight percent of the polymerizable monomer based on total weight of the monomer in the mixture.
4. The process of Claim 1 wherein the time at which the suspension is at a temperature of at least 120°C is two hours or less.
- 25 5. The process of Claim 1 wherein the conditions include maintaining the suspension at an initial temperature of at least 40°C by applying heat from an external source until the exothermic heat evolved from polymerization of the monomer to copolymer is sufficient to at least maintain the polymerization without addition of heat to the suspension.
6. The process of Claim 5 wherein the initial temperature is at least 70°C.
- 30 7. The process Claim 1 wherein the suspending medium is water.
8. The process of Claim 1 wherein the monoethylenically unsaturated monomer is present in an amount of from 20 to 99.96 weight percent based on total weight of the monomer mixture.
9. The process of Claim 1 wherein the polyethylenically unsaturated
35 monomer is present in an amount from 0.4 to 80 weight percent based on total weight of the monomer mixture.
10. The process of Claim 1 wherein the free-radical initiator is selected from peroxide, peroxyesters, azo compounds, and mixtures thereof.

11. The process of Claim 10 wherein the free-radical initiator is benzoyl peroxide, t-butyl peroctoate, t-butyl perbenzoate, and mixtures thereof.
12. The process of Claim 1 wherein the effective amount of the free-radical initiator is from 0.05 to 2.0 weight percent based on total weight of the monomer mixture.
- 5 13. The process of Claim 1 wherein the monomer mixture contains an inert diluent.
14. The process of Claim 1 wherein the monomer is imbibed into a seed polymer.
15. The process of Claim 1 wherein a portion of the monomer is added to the
10 polymerization as it proceeds.

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INTERNATIONAL SEARCH REPORT

PCT/US 93/04841

International Application No.

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C08F212/04

II. FIELDS SEARCHEDMinimum Documentation Searched⁷

Classification System

Classification Symbols

Int.Cl. 5

C08F

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched⁸**III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹**

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	GB,A,1 252 153 (THE BRITISH PETROLEUM CO. LTD.) 3 November 1971 see claims 1,2,4,14	1-15
A	US,A,3 817 965 (J.MACE) 18 June 1974 see claim 1	1

¹⁰ Special categories of cited documents : ¹⁰

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IV. CERTIFICATION

Date of the Actual Completion of the International Search

24 SEPTEMBER 1993

Date of Mailing of this International Search Report

1 2. 10. 93

International Searching Authority

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ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

US 9304841
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